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UREA PROCESS ANALYTICAL STUDY

Louis A. Dee, et al

Air Force Rocket Propulsion Laboratory
Edwards Air Force Base, California

March 1976

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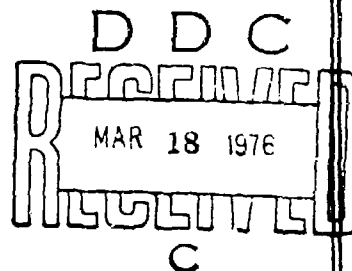
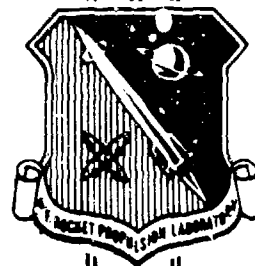
UREA PROCESS ANALYTICAL STUDY

FINAL REPORT

AUTHORS: LOUIS A. DEE
STEVEN G. WAX, LT, USAF

MARCH 1976

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AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
AIR FORCE SYSTEMS COMMAND
EDWARDS, CALIFORNIA 93523

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FOREWORD

The work described in this report was accomplished at the Air Force Rocket Propulsion Laboratory, Edwards AFB CA 93523, on Project 305810RU, "Urea Process Analytical Study". The document covers work performed from October 1975 to December 1975.

This report has been reviewed by the Information Office/DOZ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This report is unclassified, and suitable for public release.

Steven G. Wax
STEVEN G. WAX, 1st Lt, USAF
Project Engineer

Louis A. Dee
LOUIS A. DEE, GS-13
Project Chemist

Forrest S. Forbes
FORREST S. FORBES, Chief
Propellant Section

FOR THE COMMANDER

Charles E. Sieber
CHARLES E. SIEBER, Lt Colonel, USAF
Chief, Liquid Rocket Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In an effort to help determine the feasibility of the Urea process for production of the amine fuels, AFRPL established an in-house program to develop a useful analytical technique for monitoring the critical DMU → UDMH reaction. It was the absence of such a technique that presented problems for Vicksburg Chemical Company during their production contract with AFLC. Using laboratory scale equipment, AFRPL produced UDMH using purified DMU. Analysis of both reaction mixture and distillate was accomplished during all of the synthesis runs. After a variety of attempts, it was concluded that analysis of the		

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~~DMU~~ → UDMH reaction is difficult and probably not useful. Thus, great care must be taken in the scale up of the Urea process.

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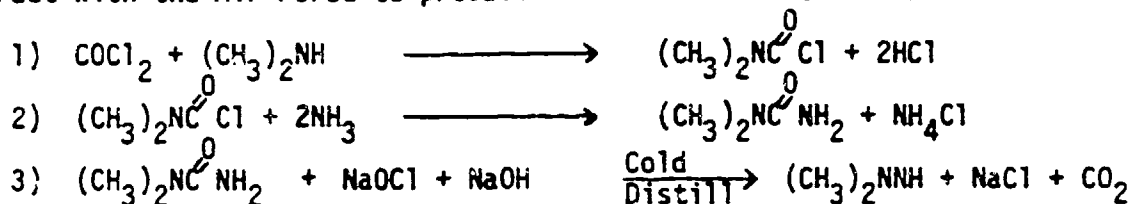
INTRODUCTION

Projected utilization of the storable amine fuels (monomethyl hydrazine, unsymmetrical hydrazine, and anhydrous hydrazine) by Government agencies is estimated to be in excess of 2,000,000 pounds per year for a minimum of a ten year period. At the present time, there are sources for all of these fuels. However, existing production methods have biologically unacceptable wastes/by-products, limited capacity and proprietary positions which make them somewhat undesirable. A requirement, therefore exists for a chemical synthesis method which can be applied to a moderate scale production of these fuels in the event current producers cannot meet Air Force and NASA requirements.

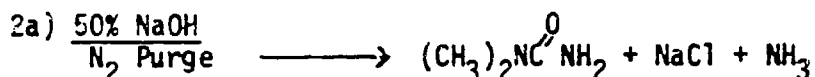
Vicksburg Chemical Company (VCC) was under contract with the Air Force to produce UDMH via the Urea Process. Although VCC failed to produce UDMH in an efficient manner, the Urea chemistry was still considered to be reasonable. Thus, the Air Force has decided to investigate the feasibility of the Urea process. As part of this plan, the AFRPL initiated an in-house project to investigate the analytical difficulties encountered by VCC during their production contract. The objective of this project was to develop a suitable analytical technique for monitoring the DMU \rightarrow UDMH reaction and if successful, to perform a limited parametric study over a range of process variables.

BACKGROUND

The Urea process, involving the oxidation of Urea with sodium hypochlorite, is one of the few commercially significant hydrazine production processes that has been successful. VCC had a production contract with the Air Force to produce UDMH via the route shown below:



For simplicity, VCC attempted initially to run the process without removing the NH_4Cl from the DMU. But, when VCC ran into problems, the presence of NH_4Cl was blamed. An additional reaction was added to react the NH_4Cl to NH_3 which would bubble out of the reaction mixture.



The laboratory experiments were very successful, resulting in high yields. Unfortunately VCC found it necessary to proceed to plant production without accomplishing pilot plant or scale-up studies. At the production scale, however, this reaction was not effective and ammonia remained during the bleaching step (reaction 3) apparently hindering the production. Next VCC used ammonia free DMU and installed additional cooling capacity to further chill the reactive mixture. It was here that they encountered their serious analytical difficulties. The yields for their parametric study were determined by measuring the UDMH concentration after three distillations. There was no way that VCC could tell what was happening during the course of the reaction. They identified no UDMH, nor any potential precursor in the reaction mixture. Thus, they could not determine the important interactions necessary to control the reaction. This made improvement of their process difficult and spelled the demise of the VCC effort.

APPROACH

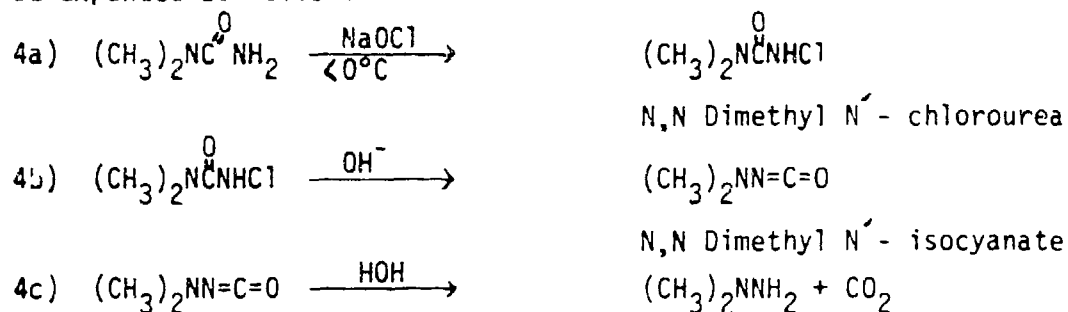
The basic approach used by AFRPL was to set up laboratory apparatus similar to that used by VCC and to run the $\text{DMU} + \text{NaOCl} \longrightarrow \text{UDMH}$ reaction. Very pure DMU was used to avoid the effects of impurities. Analysis of both the reaction mixture and distillate was accomplished. In addition, an attempt was made to understand the reaction mechanism. Following is a detailed discussion of the approach:

Purification of Dimethylurea (DMU). The DMU obtained for this program melted at $176^\circ - 179^\circ \text{C}$ as compared with a theoretical value of 182°C . The DMU was recrystallized by AFRPL from anhydrous isopropyl alcohol yielding a product which melted at $179^\circ - 181^\circ \text{C}$. Based on a range of freezing point depression constants for similar materials, the purity of the recrystallized DMU was between .006 and .002 moles of impurity/mole of DMU. This was considered sufficiently pure and the recrystallized material was used in all subsequent tests.

Reaction Equipment/Procedure. Figure 1 depicts the basic equipment used for a typical synthesis. NaOH and DMU were reacted cold ($< 0^\circ \text{C}$) and the reaction mixture was distilled using the apparatus depicted in Figure 2. Three 50-ml cuts were taken from the distillation column and analyzed for intermediates and product. Table I describes the conditions, reactant concentration and results of each run. The rationale for each run is described below. It should be noted that runs were not made for high yield, but rather for analytical purposes. Optimization of conditions and reactant concentration was generally not made except to improve the possibility of isolating an intermediate.

Isolation of Intermediates.

Reaction 3 (section 2.1) is a type of Hoffman rearrangement and may be expanded as follows:



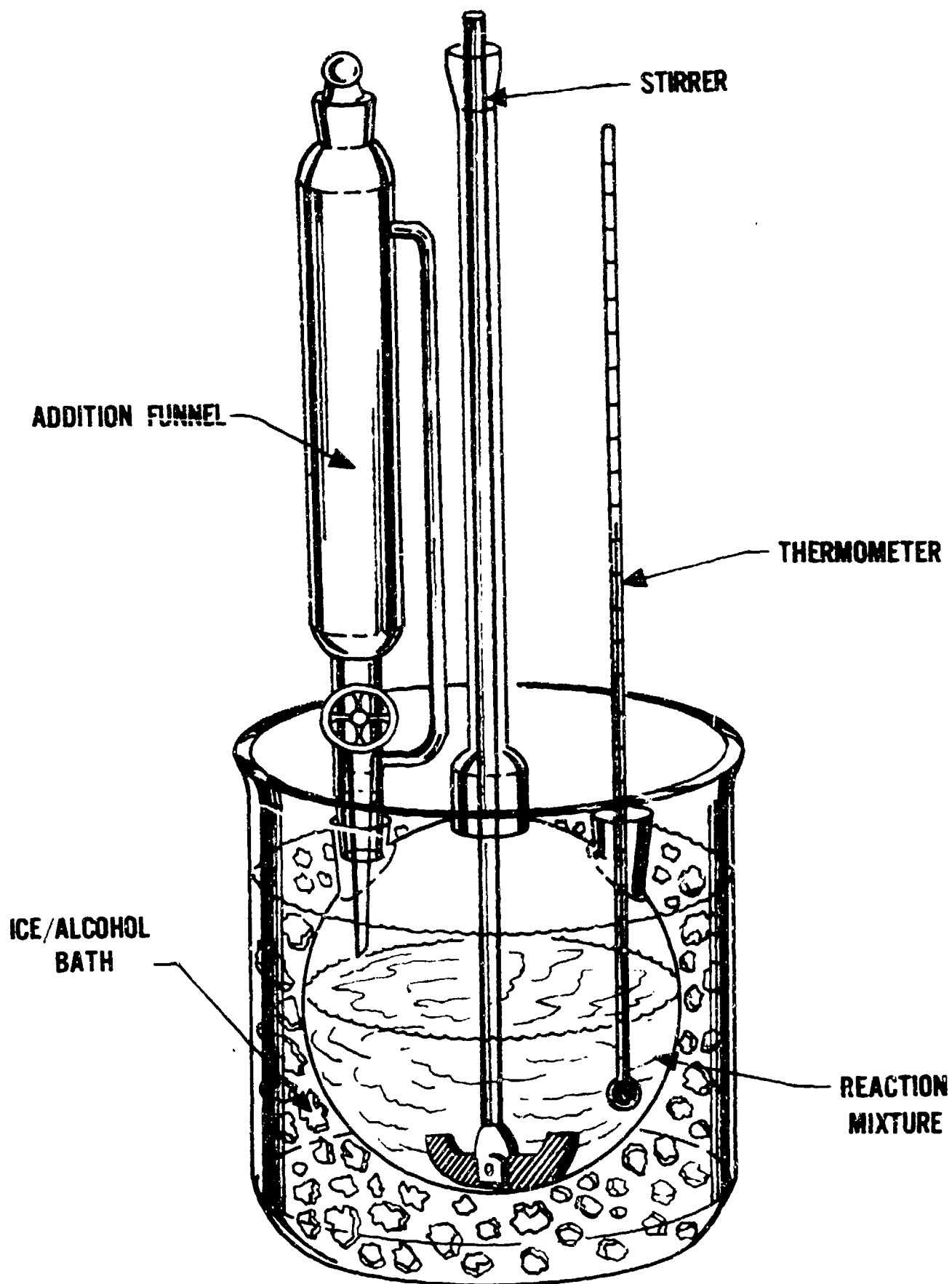


Fig. 1: REACTION APPARATUS

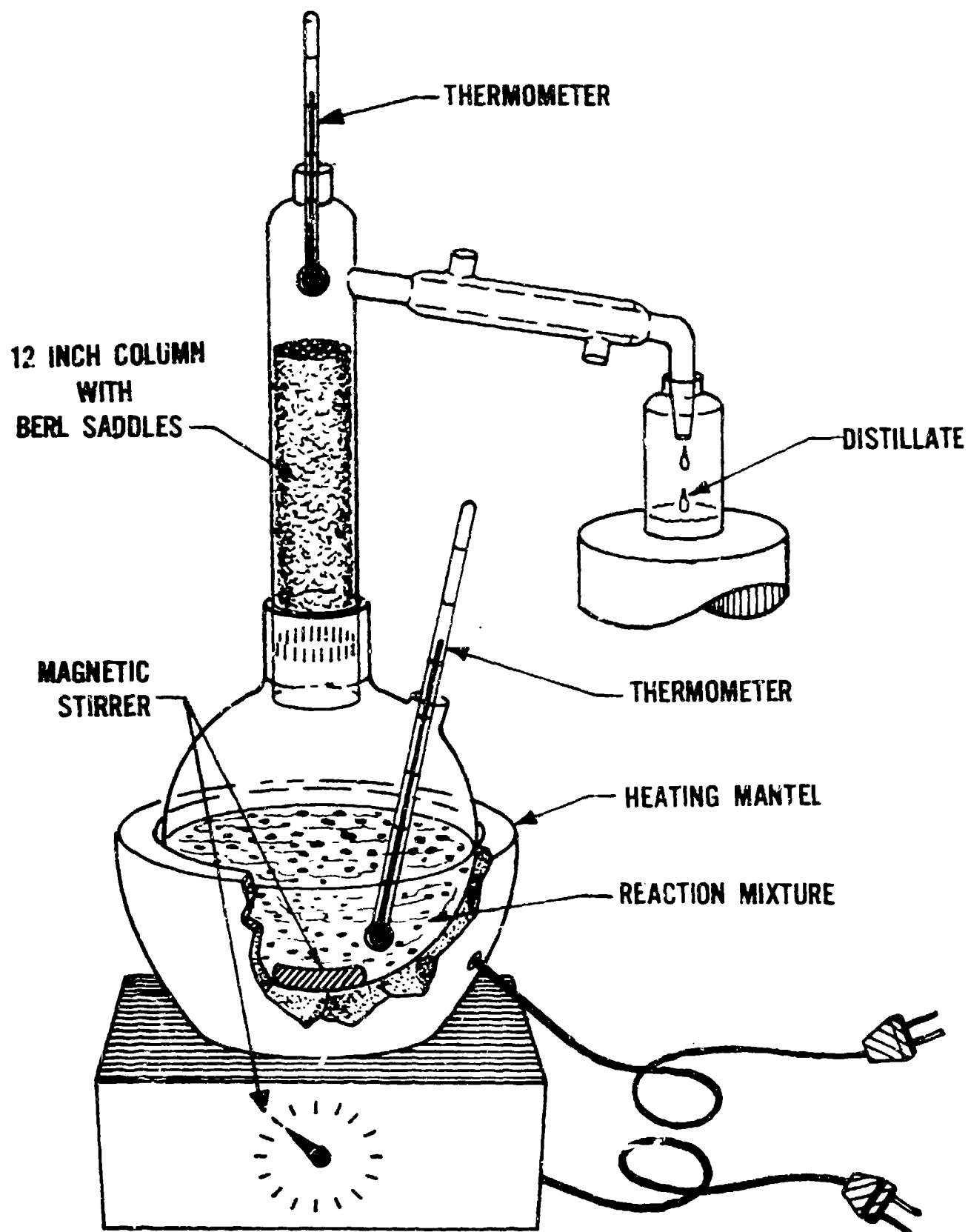


Fig. 2: DISTILLATION APPARATUS

TABLE I

Run #	Halogen/DMU	NaOH/DMU	T°C	Product Wt (g)		% Yield	Comments
				UDMH	DMH		
1	1.3/1	8/1	-5	2.9	1.2	---	CH ₂ Cl ₂ , CHCl ₃ found in distillate
2	1.3/1	8/1	-5	0.35	1.13	1.1	NaOBr used instead of NaOCl
3	1.3/1	9/1	-10	1.75	0.5	---	
4	2.6/1	4/1	-5	0.25	---	---	
5	1/1	---	-5	---	Trace	---	Ca(OCl) ₂ , CaO Used
6	1/1	2/1	-10	3.6	0.25	Trace	Aqueous phase only
7	1.3/1	8/1	-7	0.45	---	---	
8	1.2/1	2.2/1	-8	1.8	0.51	0.34	
9	1.3/1	2/1	-8	1.4	0.93	Trace	
10	1/1	2/1	-7	2.7	0.9	Trace	Dist. from CaO, no reflux
11	1/1	1/1	-7	3.3	0.5	Trace	Dist. from CaC, with reflux

A useful technique for following the rearrangement would be to monitor the formation of the isocyanate. The reaction mixture and the distillate of run #1 were examined using UV and GC (see Appendix I). Isocyanate was not found in any of the distillation cuts. The analysis of the reaction pot itself was hampered by the presence of OCl^- , since OCl^- absorbs UV very strongly. In an attempt to eliminate the very reactive hypochlorite and thus reduce the number of side reactions, a run (run #2) was made using NaOBr in place of NaOCl . Only small quantities of UDMH were formed, and no isocyanate could be found. Again UV could not be used since OBr^- also interferes. Runs #3 and #4 were at the same conditions as run 1, except that thiosulfate ($\text{S}_2\text{O}_3^{2-}$) was added to destroy the excess hypochlorite. This allowed the reaction to be monitored using UV during the distillation. Even though absorbance changes were noted, the presence of the thiosulfate was found to be detrimental to the formation of UDMH. Thus, addition of $\text{S}_2\text{O}_3^{2-}$ was abandoned.

Since it was apparent that neither the reaction mixture nor the distillate could be analyzed in a useful manner, attempts were made to improve the formation of the isocyanate in an effort to increase the probability of its isolation. A reaction with $\text{Ca}(\text{OCl})_2$ (run #5) was tried in order to use solubility as a driving force. Next, a reaction mixture was extracted cold (-10°C) with ether. Both the non-aqueous and aqueous phase (run #6) were distilled. Only the aqueous phase had product indicating that no hydrolysis occurs at the low temperature. Finally, the hydrolysis of the N-chlorourea was performed rapidly (drop by drop in steam) but no increase in yield was achieved (runs #7, 8, 9). Based on the lack of success in finding a technique for monitoring and/or isolating reaction intermediates, the work was halted at this point.

Parametric Study. Because the isolation phase of the work was not successful, no parametric studies were performed.

DISCUSSION OF RESULTS

The isolation and/or analysis of intermediates in the $\text{DMU} \rightarrow \text{UDMH}$ reaction has proven to be a very difficult chore. This difficulty is due to both the nature of the reactants and the probable mechanism of the reaction. The active specie, OCl^- , not only rearranges the DMU, but also reacts with the methyl side groups to form CHCl_3 and CH_2Cl . This, plus the strong absorption of UV by hypochlorite makes analysis of the cold reaction mixture (DMU, NaOCl , NaOH 0-10°C) impossible. The addition of the thiosulfate did destroy the excess hypochlorite; apparently it also reacts with the N-chlorourea. Since yields were affected, this technique would not be useful in monitoring the reaction.

The understanding of the mechanism of this reaction is critical to the understanding of the analytical chore. One must know where a particular product/intermediate will be found in order to analyze for it. Since UDMH was found in the distillate, but not in the reaction vessel, UDMH must be formed during the distillation. The question remains as to what precursor is in fact in the distillation feed. If it is N-chlorourea then detection and isolation would not be useful. This intermediate forms products other than UDMH (e.g., hydrazones). It is in fact not the presence of this material, but the path which it follows subsequently, that is critical in determining the UDMH yield. When reflux is accomplished prior to distillation, increasing the time of heating, the yield of UDMH is improved (runs #10,11). If an intermediate other than N-chlorourea were formed in quantity before the distillation, increased heating would not affect the yields. Isolation of N-chlorourea is useless since it does not define the yields. Since rapid hydrolysis (drop by drop) did not improve the yield, the hydrolysis is not the rate determining step. The rate determining step is the rearrangement. This occurs upon heating. No intermediates analyzed before this step are useful, after this step only products exist. It does appear from runs #1,8,9,& 10 that NaOH is only needed to hydrolyze the N-chlorourea and CaO can be used for distillation of the crude product. This should greatly reduce the by-product disposal problems.

CONCLUSION AND RECOMMENDATIONS

The foregoing indicates that analysis for the DMU→UDMH reaction intermediates is difficult and probably not useful. The reaction does produce UDMH, but it does not appear that any intermediates are of analytical value.

The lack of analytical technique for monitoring the reaction does not disprove the feasibility of the Urea process, but it does make process development of this particular reaction path more difficult. The parameters and parametric expressions used to define this reaction must be carefully selected and great care must be taken in the scale up of this process. It appears that the only clue to UDMH production is the final product. Thus tight control on reactant purity, concentrations and conditions is required to ensure that laboratory and scale-up reactions are the same.

APPENDIX I

Analytical Methods

Gas Chromatograph (GC) Analysis

GC analyses were accomplished using a Hewlett Packard 5830A Gas Chromatograph with the following devices and conditions.

Thermal Conductivity Detector	150°C
Flash Vaporizer Inlet	115°C
6' x 1/8" O.C. S/S Column	85°C
33% PEG 400/Anakrom B (90/100)	
Helium Carrier Gas	30 ml/min
Sample Size	1 μ l

Specie concentration was determined using area percent. A typical analysis is shown in Figure 3.

UV Analysis

UV analyses were accomplished with a Cary 14 UV/VIS/NIR Spectrophotometer using the following conditions.

Cell path	5 mm
Reference	H ₂ O
Spectral Region	400 - 200 nm

Pot samples were taken at successive points during the distillation and subjected to UV analysis. Absorbance data reported is the difference between the absorbance (A) at 400 nm and A at 300 nm.

POT TEMPERATURE (°C)	VOL DISTILLED (ml)	A ₄₀₀ -A ₃₀₀	%UDMH in distillate (96°-97° head Temp)
45	0	0.51	---
100	initial boiling point	0.37	---
102	20	0.4	2.6
102	65	0.12	1.6
103	95	0.13	1.0
104	125	0.12	0.2
104 (doped with 10% UDMH)	125	0.14	---

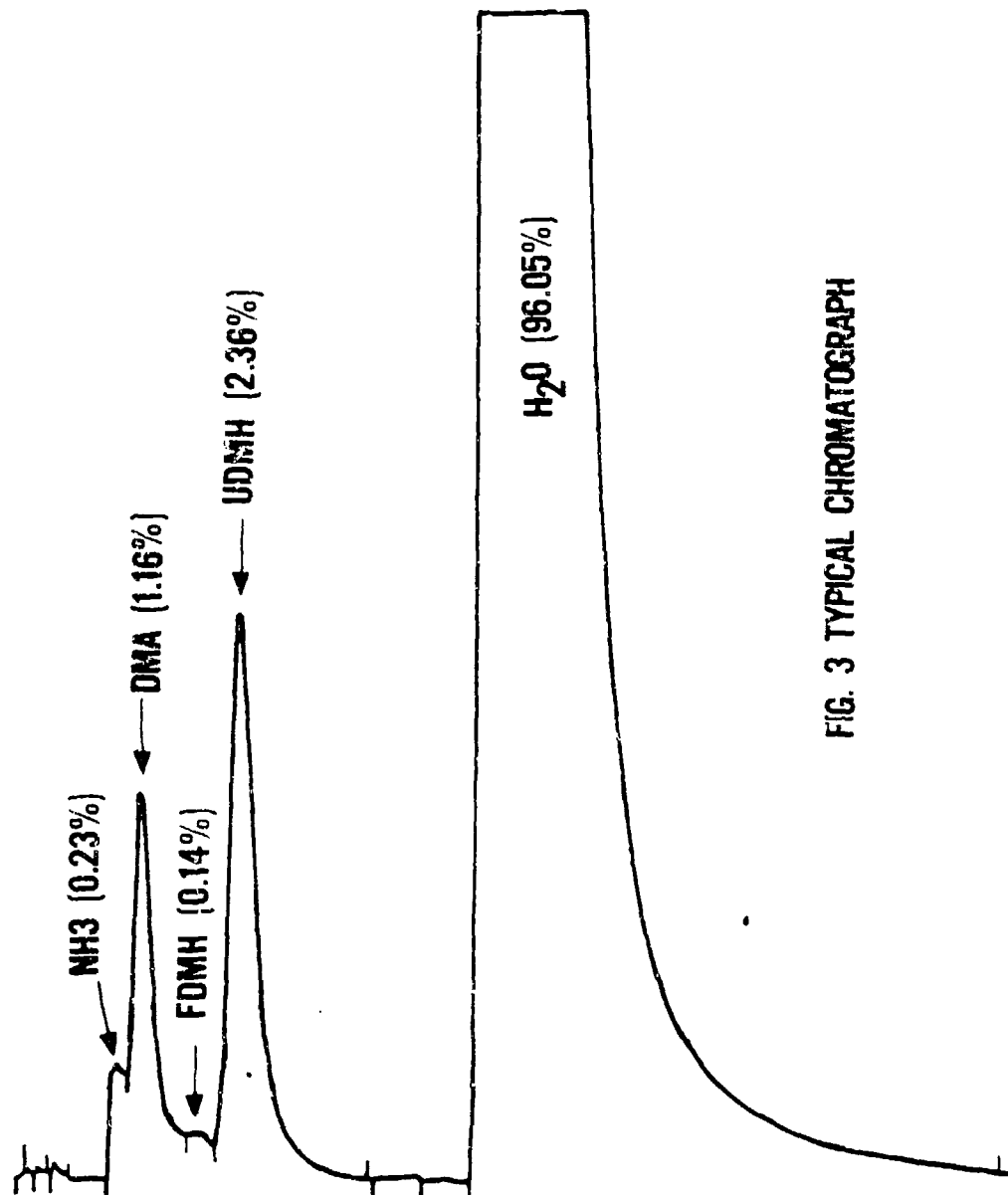


FIG. 3 TYPICAL CHROMATOGRAPH